N72-30501

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201
Telephone (614) 299-3151
Telex 24-5454

July 31, 1972

National Aeronautics and Space
Administration
Manned Spacecraft Center
R & T Procurement Branch
Houston, Texas 77058

CASE FILE COPY

Attention John E. Jones BC73(37)

Gentlemen:

Contract NAS 9-12412

Enclosed are four copies of the final report on the NASA program "Development of Nonflammable Cellulosic Foams". We are pleased to report that prototype foams have been developed with densities below 10 lb/ft^3 and with good flame resistance in oxygen-enriched atmospheres. Samples of the best formulations are being prepared and will be sent to Mr. Ballentine under separate cover.

The report contains suggestions for optimizing the most promising formulations to permit introduction of these products into ongoing NASA programs. Limited alteration of these formulations could also lead to products useful in the private sector.

We are looking forward to your comments on this project and would welcome the opportunity for further association with NASA in developing final products.

Sincerely yours,

Manfred Luttinger

Manfred Luttinger
Research Chemist
Polymer Chemistry Division

Enc.

ML:ejc

EXECUTIVE SUMMARY

Objective of Research Program

The purpose of this research was to develop cellulosic foams of minimal friability in normal handling, having densities below 10 lb/ft^3, and good flame resistance in an atmosphere of 70 percent oxygen and 30 percent nitrogen at 6.2 psia. Such compositions could find use in the Skylab program as instrument storage cushions and could be converted to civilian use for various construction applications.

Significance of Research Results

After intital investigation of halogenated foam components, which appeared quite promising, the research effort was redirected to emphasize products with minimum halogen content. Flame retardance was sought with (a) boric acid-borax mixtures, (b) reaction products of zinc chloride and ammonia, and (c) phosphoric acid-cyanamid or sulfuric acid-cyanamid derivatization of cellulose.

Decreased densities were explored by frothing techniques based primarily on commercial urea-formaldehyde foam but also utilizing aqueous colloids such as agar solutions. A major obstacle, which was overcome by the end of the project, consisted of incorporating flame retardants into the mixture without adversely affecting the frothing of the urea-formaldehyde foam system.

Satisfactory densities and flame resistance in oxygen-enriched environments were achieved with compositions containing urea-formaldehyde foam, polyvinylidene chloride latex binder, and cellulose treated with phosphoric acid-cyanamid reagent. Other compositions which were insufficiently protected for oxygen-enriched atmospheres may find application in industry where flame resistance at ambient conditions is sufficient.

Utilization of Research Results

It remains to optimize the reaction conditions for the cellulose treatment and to establish optimum levels for each component. Further gaines in lowering the density of the foams probably be achieved with the aid of auxiliary detergent-gelling components such as agar solutions. Alternative cellulose treatments and nonhalogenated binders could further improve the performance of the products.

FINAL REPORT

on

DEVELOPMENT OF NONFLAMMABLE CELLULOSIC FOAMS

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER

by

Manfred Luttinger

July 27, 1972

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201
Franklin County

TABLE OF CONTENTS

APPENDIX

FINAL REPORT

on

DEVELOPMENT OF NONFLAMMABLE CELLULOSIC FOAMS

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER

from

BATTELLE
Columbus Laboratories

July 27, 1972

INTRODUCTION

The principal objective of this program is the development of a moldable cellulosic foam for use in Skylab instrument storage cushions. Requirements include density of 10 lb/ft^3 or less, minimal friability with normal handling, and nonflammability in an atmosphere of 70 percent oxygen and 30 percent nitrogen at 6.2 psia. The best of a number of cellulosic foam formulations developed by NASA Crew Systems Division has been provided as a basis for the contract effort.

Major emphasis in the first part of the program was devoted to a study of halogenated foam components, including more highly chlorinated binders, halogen-containing additives and halogenation of the cellulose. The immediate objective was to reduce the density of the foam through reduction in inorganic phosphate without sacrificing flame-retarding properties of the foams.

The latter part of the program involved the use of frothing techniques with particular emphasis on a urea-formaldehyde foam. Halogen-containing flame retardants were deemphasized in favor of inorganic salts and the preparation of phosphate and sulphate esters of cellulose.

While NASA requirements were given first priority, utilization of foam products for civilian applications also was considered. Several of the formulations may be useful in the production of such items as ceiling tile, wall board, etc.

FUTURE WORK

The present project has resulted in cellulosic foam formulations which meet NASA's criteria for density and flammability while minimizing halogen-containing components. A number of these formulations also appear attractive for commercial applications such as acoustical ceiling tile and wall board.

The most promising foam formulations are based on a combination of treated cellulose with urea-formaldehyde foam in which is incorporated a latex binder and an auxiliary surfactant-gelling resin such as agar. While the information presented in this report clearly demonstrates the feasibility of this approach, it is recommended that these formulations be studied further in order to optimize their properties both for NASA and for commercial applications. Two lines of investigation which could not be pursued in the present program due to time and funding limitations are:

(1) Complete elimination of halogens from the formulations by substituting appropriate binders. Both latices and polymers soluble in aqueous media should be investigated. The latter are especially attractive because they may contribute to the necessary frothing of the formulation. If insolubilization after application is desired, cross-linking reactions can be employed.

(2) Investigation of alternative cellulose modifications. Phosphorylation, particularly should be studied further. Tetrakishydroxymethyl phosphonium chloride treatment and tris(aziridinyl)phosphine oxide should be investigated. Phosphorus oxychloride is an especially interesting reagent for the introduction of phosphorus into cellulose because of economic considerations.

Specific questions in the present program that remain to be answered include.

(1) What are the optimum conditions for the cyanamid-phosphoric acid reaction? Is washing out of the water soluble byproducts from this reaction desirable from the point of view of (a) increasing frothing and (b) minimizing friability and density?

(2) What is the most advantageous order of addition of the binder latex and the agar solution? What are the optimum levels of both of these?

(3) What is the optimum temperature schedule of the mixture in view of the solbility characteristics of agar and the function it performs in foam formation.

Based on the present development, we can confidently project the development of useful products for use in the Skylab program and for spinoff to industry. Optimum formulations would vary, of course, in accordance with the designated end uses of the products.

EXPERIMENTAL WORK

Halogenated Foam Components

In the process of examining the existing formulation developed by NASA, a variety of toilet tissue papers were investigated. It was understood, of course, that eventually commercial paper pulp or any other source of cellulose could be substituted. For the purposes of the laboratory work, however, toilet tissue was a convenient source of cellulose since it is easily repulped in available laboratory blendors. Moreover, this laboratory investigation could proceed from the same point of departure as the NASA formulation, which also was based on toilet tissue as the source of cellulose.

The toilet tissue papers investigated included a two-ply product by Kimberly-Clark Corporation (Kleenex) and one-ply products by Procter and Gamble (Charmin) and Scott Paper Company (Family Scott), respectively. Foams were prepared in a Waring Blendor according to formulation 5-1 (Table A-1) and dried at 75 C for 22 hours.

There was a noticeable difference in the surface hardness and stiffness of the resultant products. The foam containing the Proctor and Gamble tissue had the hardest and least resilient surface layer. The one prepared with the Scott tissue was intermediate in these properties, and the one containing the two-ply paper from Kimberly-Clark was the softest and most resilient. These differences were less noticeable on the underside of the foams which may reflect a migration of the salts towards the surface on drying. In order to standardize the method, Kleenex was used exclusively in subsequent work.

The effects of several parameters that may influence the properties of the final product were briefly explored. By varying the thickness of the casting between 1/4 and 1 inch, in formulation 5-1, the time required to dry the samples was, of course, affected, but the final products were practically identical in surface hardness and resilience. This would indicate that the cell structure is not markedly affected by the longer drying time.

Experiments 5-2, 5-3, and 5-4 in Table A-1 explore the versatility of the basic NASA formulation at lower ammonium phosphate contents. In formulation 5-2 the salt content was reduced by a factor of two without altering the other ingredients. In formulation 5-3 both the salt and water content were halfed, and in formulation 5-4 the salt content was halved and the binder level was doubled, while the total water content was reduced only slightly.

Examination of the products from the above experiments showed that resilience was only slightly improved by a decrease in the ammonium phosphate content. There may have been a slight reduction in friability because the binder was held constant resulting in an improved binder to salt ratio. While reduced salt content affected the physical properties only marginally, considerably increased stiffness was obtained at the lower water levels in the formulation. This undoubtedly affected foam density. The higher binder level in 5-4, which quadrupled the binder to salt ratio and doubled the binder to cellulose ratio as compared to 5-1, resulted in increased resilience of the product.

In general, the above experiments point to the conclusion that the physical properties of the foams apparently are not appreciably changed by fairly wide variations in the level of the ingredients. At this stage of the investigation, the objective of eliminating inorganic salts and regaining nonflammability by halogenating the cellulose was tentatively formulated. It was expected that this would lead to foams of lower density and lesser friability. Moreover, the elimination of the inorganic salts could increase the flexibility in the choice of binder, since freedom from coagulation of the binder latex by the ammonium phosphate would no longer be a criterion for binder selection. This consideration, in turn, could produce greater latitude in the flexibility and strength properties obtainable with this system. The following discussion outlines efforts to achieve these objectives prior to a discussion with the Sponsor in early May at which time the direction of the investigation was modified.

An investigation of alternative latex binders was undertaken (1) to broaden the range of obtainable physical properties and (2) to introduce more highly chlorinated polymers to optimize nonflammability. In this work the use of ammonium phosphates was continued, in case this supplementary method of flame retardance should still be necessary.

In Table A-2, the NASA formulation based on Neoprene Latex 950 is compared to two formulations employing Neoprene 400. The specific gravities for these two polymers are 1.23 and 1.42, which undoubtedly reflects a higher chlorine content for the latter. Simple substitution was not possible, however, because Neoprene 400 readily coagulated in the presence of either mono- or dibasic ammonium phosphate. This behavior is probably due to the anionic emulsifier present in Neoprene 400, while the Neoprene 950 latex, which is unaffected by phosphates, is stabilized by cationic emulsifiers. Attempts to stabilize latex 400 against phosphates with protective colloids were unsuccessful.

Another potential substitute binder investigated was Daran 220, a polyvinylidene chloride latex of 1.685 specific gravity (solids). From the nature of the polymer, this resin would be expected to produce a stiffer foam. On the other hand, if desired, it can be plasticized to produce softer, more flexible foams. Selection of halogen — or phosphorus — containing plasticizers can contribute to the flame-retarding properties of the products. Both unplasticized formulations and those plasticized with 20 weight percent of tri (2-ethylhexyl) phosphate (Flexol TOF) were prepared as shown in Table A-3.

Polyvinylidene chloride was substituted for Neoprene 950 on the basis of equal volume in formulations 8-3 and 8-4 and on an equal-weight basis in the other formulations shown in the table. The unplasticized formulations were stable but produced hard and stiff foams, as anticipated. On the other hand, the plasticized formulations (8-2 and 8-4) tended to coagulate the latex and even at the low plasticizer level produced excessively soft and weak foams. This was probably the result of latex coagulation.

Two possible solutions to these problems were indicated by the 11 series in Table A-3. The dibasic salt apparently was more compatible with the latex than the monobasic phosphate, which may be the result of its

higher pH. The addition of dilute aqueous sodium alginate seemed to improve the compatibility of the system. Use was made of this observation in latex formulations.

Another substitute binder investigated was an unplasticized polyvinyl chloride latex, FPC 790. The structure and higher polymer density (1.40) of this material suggest a higher chlorine content than Neoprene 950. The polyvinyl chloride polymer also was substituted on both an equal weight and on an equal volume basis, as shown in Table A-4. Both plasticized and unplasticized foams were prepared. Following the manufacturer's recommendation, 35 parts by weight based on polymer solids of Flexol TOF were incorporated in formulations 12-2 and 12-4. Both the unplasticized and the plasticized formulations were stable to phosphate. However, foams prepared with and without plasticizer were quite hard and stiff and either a higher plasticizer level or a more effective plasticizer may be required.

In the course of this investigation, notice was received from the manufacturer that FPC 790 had been discontinued. No further work was undertaken, therefore, with this latex. However, substitution of one of the many commercially available polyvinyl chloride latices should be possible.

In addition to binder substitution, two other methods of raising the flame retardance of the products by means of halogenated constituents were explored. These are (1) halogenation of the cellulose and (2) incorporation of halogen-containing additives.

The chemical modification of cellulose was undertaken by chlorinating tissue paper with thionyl chloride according to the method described by R. L. Boehm in J. Org. Chem. 23, 1716-20 (1958). The reaction was carried out nominally at 60 C in pyridine dried over calcium hydride. In these experiments, the recommended activation of the cellulose with 18 percent aqueous sodium hydroxide was omitted. In two separate attempts the sudden exotherm of the reaction after dropwise addition of the thionyl chloride could not be controlled, and the temperature rose to the boiling point of the mixture. The tissue paper became very deep brown as a result of the exothermic reaction. After washing with water and thorough drying

in vacuo, weight gains were measured in both runs. Elemental analysis showed 11.9 percent Cl, 2.7 percent S and 2.5 percent Cl, 3.7 percent S for the two runs respectively.

It is general knowledge that brominated materials are among the most efficient flame retardants in the class of halogenated products. One of the interesting materials in this connection is Dow Chemical's tribromoneopentyl alcohol (73.8 percent bromine). However, a high reported weight loss at relatively low temperatures (10 percent at 160 C, 90 percent at 215 C) limits the usefulness of the unmodified chemical.

A laboratory investigation was conducted to esterify tribromoneopentyl alcohol. In order to maintain the halogen content as much as possible, a highly chlorinated (57.4 percent chlorine) anhydride known as Chlorendic or HET anhydride was selected for the esterification. First attempts were to prepare the monoester with a theoretical halogen content of 32.7 percent bromine and 30.6 percent chlorine. This reaction proceeded smoothly as expected. There was some concern whether the diester could be prepared because of the possibility of steric hindrance due to the bulky halogens. However, simulation of the structure with Stuart-Briegleb molecular models indicated that diesterification should be possible. The halogen content of the pure diester would be 45.4 percent bromine and 21.2 percent chlorine. Both glassy solids and high-viscosity oils were prepared by means of these esterifications. However, the change in project emphasis (away from halogenated products) did not permit the evaluation of these materials.

Frothing Techniques

As a result of the meeting with NASA personnel mentioned earlier, it was decided to deemphasize the use of halogenated materials because of the possible formation of toxic byproducts during exposure to fire. Since the purpose of the halogenated materials was to decrease the density and friability of the existing NASA formulation by eliminating the inorganic phosphates, an alternative approach had to be formulated. It was mutually

agreed at the meeting that frothing techniques will be investigated with the objective of lowering the foam density. If necessary, the ammonium phosphate could be replaced by other nonhalogenated fire retardants, preferably organic phosphates. However, a small amount of halogenated binder, as represented by the Neoprene latex, could be tolerated.

Attention was focused on a urea-formaldehyde foam of low density developed in Germany under the trade name "Isoschaum". This material is produced in this country by U. F. Chemical Corporation of Woodside, New York, under the trade name "U.F.C.-Foam" and is used primarily for thermal insulation and sound absorption. According to the manufacturer, U.F.C.-Foam has the following suggested specifications:

Fire Behavior:	ASTM D 1692 Self Extinguishing ASTM E 136 Noncombustible	
Flame Spread:	ASTM E 84	
	Noncombustible	25
	Smoke Density	0-5
	Fuel Contributed	10
Density:	0.6 lb/cu ft	
Sound Absorption:	83-92 percent at 400-3200 cps for 2 inch thickness.	

It is produced by frothing a detergent solution containing a gelling agent for the resin, followed by mixing of the froth with the aqueous urea-formaldehyde dispersion. This results in a stiff foam which loses essentially all its water within 1 or 2 days at room temperature. For commercial applications a specially designed spray gun is used. In the laboratory any convenient frothing technique can be used.

Foams could be readily produced in a Waring Blendor by frothing the detergent solution to a "standing" foam (one that does not quickly collapse when agitation is discontinued) and adding the aqueous urea-formaldehyde dispersion. Set-up times were faster than anticipated (30 to 45 seconds), leaving little time for mixing and casting. The cast foam retains its shape during water evaporation. Forced drying at elevated temperatures causes shrinking, but some oven drying became necessary when the cellulose was incorporated.

In order to combine the UFC foam with NASA's cellulosic-foam formulation, the interaction of various components with the UFC foam were studied. A number of these formulation modifications are outlined in Table A-5.

It was very encouraging to be able to demonstrate in formulation 25-1 that the UFC foam could be modified with a substantial quantity of water without impairing its physical properties. On the other hand, addition of soluble ionic fire retardants (25-2 to 25-4) destroyed the frothing properties of the detergent solution, regardless of the mode of addition. Clearly, some other fire-retardant system than the one used in the prototype NASA formulation will have to be employed.

Experiments 25-5, 28-1, and 30-1 explored the interaction of three other types of fire retardants with UFC foam. These are antimony trioxide, a substantially insoluble inorganic oxide; Tyzor AA, an organic titanate; and FR-2406, tris (2,3-dibromopropyl) phosphate, which could act as a plasticizer for polyvinyl or polyvinylidene chloride. Of these additives, both the antimony trioxide and Tyzor AA were compatible with the UFC foam, while FR-2406 destroyed the foaming action of the detergent solution. The presence of antimony trioxide did cause a moderate increase in the fluidity of the foam, which may be attributable to a possible increase in its cell size. Regarding the FR-2406, it is, of course, possible that its incorporation into a latex or attachment to the cellulose could eliminate the detrimental effect it produces on the UFC foam.

Another avenue to incorporating additives into the UFC foam is to reinforce the detergent with additional surfactants, particularly ones with strong foaming or foam-stabilizing properties (see 25-6 in Table A-5). The original intention was to use Atlox 3409F (anionic-nonionic blend) to emulsify the FR-2406, for which it was specifically recommended. However, when it was found that this surfactant blend interfered with the foaming action of the UFC detergent solution, a cationic surfactant, Amine O (heterocyclic tertiary amine alkylated with oleic acid), was tried. This material formed a precipitate with the detergent solution and prevented foam formation. Two more attempts

were made with nonionic surfactants (Monamid CMA, a cocoanut monoethanolamide recommended as a foamer, and Alrosol S, a fatty alkylolamide condensate recommended as a stabilizer) but again with negative results. It would appear that the search for a surfactant compatible with the detergent solution would require an extended effort which was not feasible within the objectives and time table of the program.

Since it was unlikely that UFC foam could be used as the sole binder to provide the desired strength properties of the finished product combinations of UFC foam with latices were investigated as summarized in Table A-6. Incorporation of Neoprene 950 at two concentration levels caused collapse of the foam and resulted in relatively high-density products. On the other hand, addition of Neoprene 400 did not interfere with the foam formation, but the dried product was distinctly weaker than the unmodified UFC foam. Similarly, Daran 220 was compatible with foam formation but produced a more open and weaker foam structure. It must be borne in mind however, that the unmodified UFC foam is not a very strong structure and that its function in the cellulosic foam will be primarily to lower density. Strength properties will be sought from the cellulose and the latex binder.

The experiments in Table A-7 represent an attempt to incorporate into the UFC foam a colloid that could be useful in protecting latices from premature coagulation. Moreover, being readily gelled under acid conditions, the alginates were thought to aid in air entrainment and thus contribute to lowering the density of the final product. Therefore, the low-viscosity solution of 1 percent Kelgin LV was compared to both a high-viscosity, high-solids solution of 5 percent Kelgin LV and to a high-viscosity, low-solids solution of 1 percent Superloid.

Addition of these algimates did not seem to greatly affect either foam formation or the properties of the UFC foam. They should, therefore, be suitable as protective colloids and could possibly be useful in cellulosic foam formation. However, they produced very poor UFC foam products in combination with either the organic titanate (Tyzor AA) or the latex plasticizer, tricresylphosphate.

Several experiments were conducted with the goal of incorporating untreated cellulose into UFC foam (see Table A-8). In the first three experiments shown in the table, both the water to cellulose and the resin to cellulose ratios were progressively increased. This resulted in progressively lower density and decreased strength and demonstrated that the cellulose contributes more to the strength of the products than does the urea-formaldehyde resins. The remaining two experiments in Table A-8 were conducted to show the effect of polyvinylidene chloride latex and sodium alginate on these products. The alginate contributed to decreased foaming and, consequently, to a higher density and increased strength.

UFC foam, although noncombustible at ambient conditions, does burn in atmospheres of elevated oxygen content and cannot protect the cellulose. Consequently, several nonhalogen treatments for the cellulose were investigated. These are shown in Table A-9.

The first four reactions in the table describe the preparation of inorganic cellulose esters such as phosphates (35-1 to 35-3) and sulphates (35-4). The reactions were carried out according to patents issued to Courtaulds Ltd.[1] and to Joseph Bancroft and Sons Co.,[2] and reviewed by Ward[3]. Experiment 35-1 was not completed because of insufficient solubility of the ingredients. The other two phosphate reagents dissolved with some difficulty, while the sulphate reagent dissolved readily. The cellulose was soaked in the reagents and the moisture was removed by heating at 50 C for 24 hours. The treated paper then was exposed for 15 minutes at 105 C. The washing step in dilute alkali, which is prescribed for fabric treatment, was omitted because soluble residues in the foam are not necessarily detrimental and may in fact improve flame resistance.

Other treatments shown in Table A-9 are nonpermanent in the sense that, like the NASA formulation, physical deposition of flame retardants rather than chemical reaction of the cellulose is involved. Experiments 37-1 and 37-4 represent different levels of boric acid-borax mixtures in accordance with recommendations by Ramsbottom and Snoad[4]. On setting, this mixture forms a glass rather than a crystalline solid and is expected

to result in less friable foams. Experiments 37-3 and 37-5 deposit the reaction product of zinc chloride and ammonia in the cellulose in accordance with a patent issued to Ferguson and Pyrene Manufacturing Co.[5] The products reportedly formed are zinc amines of the formula $ZnCl_2 \cdot XNH_3$. These last two experiments are essentially repetitions of the same procedure. The cellulose was soaked in the zinc chloride solution and subsequently contacted with ammonia, which caused precipitation of salts in the cellulose. Unlike the esterification reactions, the last four experiments required water removal only and this was accomplished by heating at 50 C for up to 24 hours. All of the treated papers showed significant weight gains. These were greatest in the esterification experiments which employed high loadings of inorganic and organic chemicals.

The combination of the treated cellulose with UFC foam is described in Table A-10. Formulation 34-1 of Table A-8 was used as a point of departure. The general procedure was to pulp the tissue paper with water in a Waring Blendor, to add the detergent solution and whip up as much foam as possible, and, finally, to mix in the urea-formaldehyde dispersion. The mass was poured into polyethylene-lined trays within 30 to 60 seconds of the resin addition. In experiment 40-2, the latex was added to the pulped cellulose before the addition of the detergent solution. Similarly, in experiment 41-1 the hot agar solution was added to the pulped cellulose before the addition of the detergent. Most mixtures reached somewhat elevated temperatures during pulping. This may account for the excess water observed after casting most of these masses, since the foam probably was less stable at the elevated temperature than it may have been otherwise.

The densities of the foams from 38-3 and 38-4 are considerably higher than desirable (10 lb/ft^3), because of greater shrinkage during drying than was the case in the other experiments in Table A-10. Formulations 38-1, 38-2, and 40-2 are fairly close to the desired density. Since the base formulation (34-1) has a density of 6.2, the increase in the above foams must be due to the added flame retardants, either because of their direct contribution to weight or due to their foam-depressing effect. It is

particularly noteworthy therefore that a very low density could be achieved in 41-1 which contained an agar solution. By increasing the viscosity and stiffening the foam produced in the Waring Blendor, agar resin prevented the collapse of the structure on drying. Since the agar has been reported to have independent foaming ability, this may be another way in which the material contributes to low density. Since agar is an expensive product, it will be necessary eventually to establish the minimum effective level, or to find lower-cost substitutes.

Flammability testing of cellulosic foams was carried out using test atmospheres of 60, 70, and 100 percent oxygen content at atmospheric pressures in a test chamber having a volume of 2.5 to 3.0 cubic feet. Samples were cut in 5-inch lengths with thicknesses and widths varying between 7/16 and 5/8 inches and between 3/4 and 1-1/2 inches, respectively. Each was mounted upright in direct contact with the ignition source which consisted of a michrome wire wrapped with 1/2 of a two-ply toilet tissue ($\sim$ 0.2g). Gas was introduced at 3 ft^3/min for 60 and 100 percent oxygen atmospheres and at 2.4 ft^3/min for the 70 percent oxygen atmosphere, and the samples were left in contact with the test atmosphere for 5 minutes before ignition.

According to the data summarized in Table A-11, formulation 40-2 had the best flame-retarding properties. It did not ignite in any of the three test atmospheres. At ambient conditions in the laboratory this sample picked up 10 percent moisture. However, the flame retarding properties are not dependent on moisture content, since freshly oven-dried samples passed the flammability test at 100 percent oxygen. The density of this formulation is approximately 10 lb/cubic foot and the foam is not very friable and has fairly good integrity. Formulation 40-2 is recommended, therefore, as the product meeting the essential requirements. However, since the flammability is better than necessary, it should be possible to produce a similar formulation with somewhat reduced fire-retardant content which still would be expected to meet the nonflammability standard but which would be lower in density.

The next best formulation in terms of fire retardance is 38-1. It contains less phosphoric acid-cyanamid reagent and does not have any polyvinylidene chloride binder (unlike 40-2). Its structure collapsed more on drying than did that of 40-2, which accounts for its higher density, and its reduced fire retardants level is mirrored in its lower fire resistance.

Formulations 38-3 and 38-4 (sulfuric acid-cyanamid treated and zinc chloride-ammonia-reagent treated, respectively,) also exhibited fire-retarding properties at elevated oxygen content but to a lesser extent than the foams described earlier. It may be especially interesting for civilian applications that most of the foams based on the urea-formaldehyde system were fire retardant at atmospheric conditions. Only 26-1 and 26-2 with increased cellulose-to-resin ratios had reduced fire retardancy. In view of the low cost of the raw materials, this should be a very attractive product for the civilian market.

ML:ejc
July 31, 1972

REFERENCES

1. Brit. Patent 634,690 (to Courtaulds Ltd.)

2. Brit. Patent 604,197 (to Joseph Bancroft & Sons Co.)

3. Ward, F. J. Soc. Dyers and Col. 71, No. 10, 569-78, October, 1955.

4. Department of Scientific and Industrial Research "Second Report of the Fabrics Coordinating Research Committee (London: H.M.S.O. 1930) pp. 54 et seq.

5. U. S. Patent 1,261,736; April 2, 1918 (to Ferguson and Pyrene Manufacturing Co.)

APPENDIX

TABLE A-1. BASIC VARIATIONS IN THE PREFERRED NASA FORMULATION

Ingredient[b] \ Formulation	5-1[a]	5-2	5-3	5-4
	Weight, grams			
Tissue Paper	100	100	100	100
Neoprene Latex 950	150	150	150	300
Thiocarbanalide	5	5	5	10
$NH_4H_2PO_4$	150	75	75	75
Water	600	600	300	445

[a] NASA Crew Systems Division formulation except for the water content which was undefined.

[b] Description of proprietary materials appears in Table A-12.

TABLE A-2. VARIATION IN NEOPRENE LATEX BINDER

Ingredient \ Formulation	5-1[a]	7-1	7-2
	Weight, grams		
Tissue Paper	100	100	100
Neoprene Latex 950	150	--	--
Neoprene Latex 400	--	150	150
Thiocarbanalide	5	5	5
$NH_4H_2PO_4$	150	150	--
$(NH_4)_2HPO_4$	--	--	150
Water	600	600	600

[a] NASA Crew Systems Division formulation except for the water content which was undefined.

TABLE A-3. INVESTIGATION OF POLYVINYLIDENE CHLORIDE LATEX BINDER

Ingredient \ Formulation	13-1[a]	8-1	8-2	8-3	8-4	11-1	11-2	11-3
	Weight, grams							
Tissue Paper	100	100	100	100	100	100	100	100
Neoprene 950	150	--	--	--	--	--	--	--
Daran 220	--	123	123	169	169	123	123	123
Flexol TOF	--	--	15	--	20.6	--	--	--
Superloid (1% aqueous)	--	--	--	--	--	--	150	150
$NH_4H_2PO_4$	150	150	150	150	150	--	150	150
$(NH_4)_2HPO_4$	--	--	--	--	--	150	--	--
Water	1173	1200	1185	1246	1225	1200	1050	1200
pH	←3-3.5→					6	3.5	4

[a] NASA Crew Systems Division formulation except for the water content which was undefined.

TABLE A-4. INVESTIGATION OF VINYL CHLORIDE LATEX BINDER

Ingredient \ Formulation	12-1	12-2	12-3	12-4
	Weight, grams			
Tissue Paper	100	100	100	100
FPC 790	150	150	171	171
Flexol TOF	--	26.2	--	30.2
$NH_4H_2PO_4$	150	150	150	150
Water	1173	1147	1152	1122
pH	<—— 3-3.5 ——>			

TABLE A-5. INTERACTION OF UFC FOAM WITH ADDITIVES

Ingredient \ Formulation	25-1	25-2	25-3	25-4	25-5	28-1	30-1	25-6
	Weight, grams							
Detergent	50	50	50	50	50	50	50	50
UFC Resin	50	50	50	50	50	50	50	50
Water	50		40	50	50			50
$NH_4H_2PO_4$		10						
NH_4PF_6			10	3.3				
Sb_2O_3					6.7			
Tyzor AA						2		
FR-2406							4	
Surfactant[(a)]								3.3

(a) A variety of surfactants were tested in this formulation, including Atlox 3409.F, Amine O, Monamid CMA and Alrosol S.

TABLE A-6. INTERACTION OF UFC FOAM WITH LATICES

Ingredient \ Formulation	24-1[a]	24-2	24-3	24-4	39-1
	Weight, grams				
Detergent	50	50	50	50	50
UFC Resin	50	50	50	50	50
Neoprene 950	--	50	20	--	--
Neoprene 400	--	--	--	20	--
Daran 220	--	--	--	--	20

(a) Unmodified UFC Foam as recommended by U.F. Chemical Corp.

TABLE A-7. INVESTIGATION OF ALGINATES IN UFC FOAM

Ingredient \ Formulation	28-2	30-2	31-1	31-2	30-3	30-4
	Weight, grams					
Detergent	50	40	40	40	40	40
UFC Resin	50	50	50	50	50	50
Kelgin LV, 1 percent aqu.	4	10			10	10
Kelgin LV, 5 percent aqu.				10		
Superloid, 1 percent aqu.			10			
Tyzor AA					4	
Tricresyl phosphate						4

TABLE A-8. INCORPORATION OF CELLULOSE INTO UFC FOAM

Ingredient \ Formulation	26-1	26-2	34-1	40-1	34-2
		Weight, grams			
Tissue Paper	25	50	25	25	25
Detergent	50	200	200	200	200
UFC Resin	50	200	200	200	200
Water	100	500	500	484	400
Daran 220	--	--	--	41	
Kelgin LV, 5 percent aqu.	--	--	--	--	100
Density, lb/cu ft	14.1	8.3	6.2	≈7[a]	9.1

[a] Very uneven casting made exact density determination impossible.

TABLE A-9. TREATMENT OF CELLULOSE WITH FIRE RETARDANTS

Ingredient \ Formulation	35-1	35-2	35-3	35-4	37-1	37-4	37-3	37-5
	Weight, grams							
Tissue Paper	25	25	25	25	25	25	25	25
Water	77	77	28	113.5	192	184	50	50
H_3PO_4, conc.	20	20	20					
H_2SO_4, conc.				16.5				
$(NH_4)_2HPO_4$	28							
$NH_4H_2PO_4$		28	28					
$(NH_4)_2SO_4$				10				
Cyanamid-50	50	75	124	60				
H_3BO_3					1.5	3.0		
$Na_2B_4O_7 \cdot 10H_2O$					6.5	13.2		
$Zn\ Cl_2$							18	18
NH_3, 29 percent aqu.							90	90
Weight Gain of Treated Paper								
grams	--	98.2	110.3	71.4	4.5	10.6	20.2	21
percent	--	393	440	286	18	42	81	84

TABLE A-10. INCORPORATION OF TREATED CELLULOSE INTO UFC FOAM

Ingredient / Formulation / Cellulose Treatment[(a)]	38-1 35-2	38-2 35-4	38-3 37-3	38-4 37-4	40-2 35-3	41-1 37-1
	Weight, grams					
Treated Tissue Paper	123	96	45	36	135	29.5
Detergent	200	200	200	200	200	200
UFC Resin	200	200	200	200	200	200
Water	500	500	500	500	500	400
Daran 220	--	--	--	--	41	--
Agar, 5 percent aqu.	--	--	--	--	--	100
Density, lb/cu ft	11.5	9.8	14.6	14	9.6	5.6

(a) See Table A-9.

TABLE A-11. FLAMMABILITY AND DENSITY MEASUREMENTS OF CELLULOSIC FOAMS

Foam Formulation	Density lb/ft^3	Flame Propagation[a] Ambient Atmosphere[b]	60% O_2	70% O_2	100% O_2
26-1	14.1	F	F		
26-2	8.3	S	F		
34-1	6.2	N	F		
34-2	9.1	N	F		
38-1	11.5	N	N	F	
38-2	9.8	N	S		
38-3	14.6	N	S	F	F
38-4	14.0	N	F	F	F
40-1	≈7[c]	N	F[d]		
40-2	9.6	N	N	N	N
41-1	5.6	N	F		

[a] Carried out at ambient pressure.
N = nonflammable; S = self extinguishing; F = flammable.

[b] 21 percent oxygen at ambient pressure.

[c] Very uneven casting made exact density determination impossible.

[d] Irregular test sample; burned for some time before becoming extinguished.

TABLE A-12. SOURCE AND DESCRIPTION OF PROPRIETARY MATERIALS

Material	Description	Supplier
Alrosol S	Surfactant; fatty alkylolamide condensate	Ciba-Geigy
Amine O	Surfactant; heterocyclic tertiary amine	Ciba-Geigy
Atlox 3409F	Surfactant; anionic/nonionic blend	ICI America
Cyanamide-50	Hydrogen Cyanamide, 50% H_2NCN	American Cyanamid
Daran 220	Polyvinylidenechloride latex, 60% solids	W. R. Grace
Flexol TOF	Plasticizer, tri(2-ethylhexyl)phosphate	Union Carbide
FPC-790	Polyvinyl chloride latex, unplasticized, 50% solids	Firestone
FR-2406	Fire retardant additive, tris(2,3-dibromo-propyl)phosphate	Dow
Kelgin LV	Sodium alginate, low viscosity	Kelco
Monamid CMA	Surfactant, coconut monoethanolamide	Mona Industries
Neoprene 400	Polychloroprene latex, 50% solids, anionic	DuPont
Neoprene 950	Polychloroprene latex, 50% solids, cationic	DuPont
Superloid	Ammonium Alginate, high viscosity	Kelco
Tyzor AA	Titanium acetylacetonate	DuPont
UFC Resin	Modified urea-formaldehyde dispersion, 44% solids	U.F. Chemical Corp. Woodside, N.Y.